Describing Spin-Selective Reactions of Radical Pairs Using Quantum Jump Approaches

Alpha Lee*

(Dated: 10 Oct 2011)

Abstract

Recently, spin-selective radical pair reactions have been studied using concepts from quantum measurement theory. In this Article, we show that the approach taken by Kominis (Physical Review E, 83, 2011, 056118) leads to erroneous results due to a problematic treatment of quantum jumps. Correct consideration of quantum jumps leads to either the traditional master equation or the Jones-Hore master equation.

*Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ; Department of Chemistry, Faculty of Natural Sciences, Imperial College London, London SW7 2AZ; Electronic address: alpha.lee09@imperial.ac.uk

I.   INTRODUCTION

Spin-selective radical–ion pair reactions are at the core of spin chemistry. The phenomenological master equation [1] (1) is often used to model spin-selective reactions.

$$\frac{d\rho}{dt} = -i[H, \rho] - \frac{k_S}{2}\{Q_S, \rho\} - \frac{k_T}{2}\{Q_T, \rho\}$$ (1)

where ρ is the density matrix of the reactants, $\{\}$ denotes the anti-commutator, H is the Hamiltonian describing unitary evolution of the radical pair, k_S and k_T are the rates of reaction through singlet and triplet channels respectively, and Q_S and Q_T are singlet and triplet projection operators respectively. Recently, based on quantum measurement theory, Kominis [2, 3] derived equation (2) and quantum jump equations (3) and (4)

$$\frac{d\rho_{nr}}{dt} = -i[H, \rho] - \frac{k_S + k_T}{2}(\rho Q_S + Q_S \rho - 2Q_S \rho Q_S)$$ (2)

ρ_{nr} describes the state of the radical pairs before recombination. Equation (2) is derived by making the analogy between spin-selective chemical reaction and electron tunneling in a quantum dot. The quantum non-demolition measurement of the quantum dot causes the wavefunction to collapse periodically, thus pure decoherence without energy dissipation is observed. Kominis then introduced quantum jumps (3) and (4), where p_S is the probability of reacting down the singlet channel and p_T is the probability of reacting down the triplet channel, to represent chemical reaction.

$$p_S = k_S \langle Q_S \rangle dt$$ (3)

$$p_T = k_T \langle Q_T \rangle dt$$ (4)

This an erroneous application of the Bohr-Einstein quantum jump [4] and leads to misinterpretation of the "no jump" event [5] which will be analysed below. Subsequently, Kominis [6] introduced a revised master equation based on a phenomenological interpolation between the "maximal coherence case" and the "minimal coherence case" without correcting the underlying physics in (3) and (4). Rephrasing the argument presented, singlet-triplet coherence is measured by the parameter ρ_{coh}.

$$\rho_{coh} = \frac{Tr\{\rho_{ST}\rho_{TS}\}}{Tr\{\rho_{SS}\}Tr\{\rho_{TT}\}}$$ (5)

2

where $\rho_{ST} = Q_S\rho Q_T$, $\rho_{TS} = Q_T\rho Q_S$, $\rho_{SS} = Q_S\rho Q_S$ and $\rho_{TT} = Q_T\rho Q_T$. The evolution of the density matrix is given by

$$\frac{d\rho}{dt} = -i[H,\rho] - \frac{k_S+k_T}{2}(\rho Q_S + Q_S\rho - 2Q_S\rho Q_S) - (1-\rho_{coh})\frac{d\rho_{incoh}}{dt} - \rho_{coh}\frac{d\rho_{coh}}{dt} \quad (6)$$

$$d\rho_{incoh} = k_S dt Q_S\rho Q_S + k_T dt Q_T\rho Q_T \quad (7)$$

$$d\rho_{coh} = (k_S Tr\{Q_S\rho\} + k_T Tr\{Q_T\rho\})dt\frac{\rho}{Tr\{\rho\}} \quad (8)$$

The interpolation parameter ρ_{coh} is introduced "by hand" and the limiting cases of the resulting equation will be commented on below. This Article will also show how consistent derivation of the master equation points towards (9), the Jones-Hore master equation [7] or the phenomenological master equation.

$$\frac{d\rho}{dt} = -i[H,\rho] - \frac{k_S}{2}\{Q_S,\rho\} - \frac{k_T}{2}\{Q_T,\rho\} - \frac{k_S+k_T}{2}(\rho Q_S + Q_S\rho - 2Q_S\rho Q_S) \quad (9)$$

A microscopic derivation of (1) has been reported by Ivanov et al. [8]. Appendix A contains the full microscopic derivation of (9).

II. COMMENT ON THE KOMINIS MASTER EQUATION

A. Problem with "no jump" events

The quantum jump equations (3) and (4) fail to capture the physical significance of a no-jump event. In a qualitative sense, a no-jump event represents either the wavefunction is still in $\{S,T\}$ subspace or, importantly, the fact that the radical pair has already reacted [9, 10]. If one starts observing the system at time t and does not see the system executing a quantum jump after a very long time, one should conclude that the system has already jumped at some prior time before the observation rather then believing that the system is yet to jump. To capture this, a non-Hermitian term must be added to the Hamiltonian

$$H_{eff} = H - i\frac{k_S}{2}|S\rangle\langle S| - i\frac{k_T}{2}|T\rangle\langle T| \quad (10)$$

Putting into (2) the non-Hermitian Hamiltonian (10), which corresponds to quantum jump equations (3) and (4), and only considering the S-T subspace

3

$$\frac{d\rho}{dt} = \frac{d\rho_{reaction}}{dt} + \frac{d\rho_{nr}}{dt}$$

$$= -i[H - i\frac{k_S}{2}|S\rangle\langle S| - i\frac{k_T}{2}|T\rangle\langle T|, \rho] - \frac{k_S + k_T}{2}(\rho Q_S + Q_S\rho - 2Q_S\rho Q_S)$$

$$= -i[H, \rho] - \frac{k_S}{2}\{Q_S, \rho\} - \frac{k_T}{2}\{Q_T, \rho\} - \frac{k_S + k_T}{2}(\rho Q_S + Q_S\rho - 2Q_S\rho Q_S)$$

and the Jones-Hore master equation [7] is recovered.

The role of the non-Hermitian Hamiltonian can be seen more clearly when one writes the jump-free evolution of the system explicitly. When $\|H_{eff}\| dt \ll 1$

$$|\psi(t + dt)\rangle = e^{-iH_{eff}dt}|\psi(t)\rangle$$

$$\approx (1 - iH_{eff}dt)|\psi(t)\rangle \tag{11}$$

ignoring second order terms in dt

$$|\psi(t + dt)|^2 = \langle\psi(t)|(1 + iH_{eff}^+ dt)(1 - iH_{eff}dt)|\psi(t)\rangle$$

$$= 1 - \delta p \tag{12}$$

where δp is the decrease in the norm of the wavefunction which is compensated by the jump to products. Identifying δp as the probability of a quantum jump

$$\delta p = idt\langle\psi(t)|H_{eff} - H_{eff}^+|\psi(t)\rangle$$

$$= dt(k_S\langle\psi(t)|Q_S|\psi(t)\rangle + k_T\langle\psi(t)|Q_T|\psi(t)\rangle)$$

$$= k_S dt\langle Q_S\rangle + k_T dt\langle Q_T\rangle \tag{13}$$

This shows qualitatively that although the jump operators "fill up" the states representing the reaction products (S_0 and T_0), the populations of the radical pair S and T states are only "removed" by the non-Hermitian Hamiltonian.

From an algebraic perspective, any completely positive Markovian evolution can be written in the Lindblad form

$$\frac{d\rho}{dt} = -i[H, \rho] + D(\rho)$$

$$= -i[H, \rho] + \sum_i L_i\rho L_i^+ - \frac{1}{2}\{L_i^+ L_i, \rho\} \tag{14}$$

where L_i are Lindblad operators. The formal solution to (14) can be written as

$$\rho(t) = e^{\hat{\hat{L}}t}\rho(0) \tag{15}$$

$\hat{\hat{L}}$ is a superoperator that can be written trivially in terms of the jump superoperator $\hat{\hat{J}}$

$$\hat{\hat{L}} = \hat{\hat{J}} + \hat{\hat{L}} - \hat{\hat{J}} \tag{16}$$

using an identity for superoperators [11]

$$e^{(\hat{a}+\hat{b})x} = \sum_{k=0}^{\infty} \int_0^x dx_k \int_0^{x_k} dx_{k-1}... \int_0^{x_2} dx_1 e^{\hat{a}(x-x_k)}\hat{b}e^{\hat{a}(x_k-x_{k-1})}\hat{b}...\hat{b}e^{\hat{a}x_1} \tag{17}$$

$$e^{(\hat{\hat{J}}+\hat{\hat{L}}-\hat{\hat{J}})t}\rho(0) = \sum_{k=0}^{\infty} \int_0^t dt_k \int_0^{t_k} dt_{k-1}... \int_0^{t_2} dt_1 e^{(\hat{\hat{L}}-\hat{\hat{J}})(t-t_k)}\hat{\hat{J}}e^{(\hat{\hat{L}}-\hat{\hat{J}})(t_k-t_{k-1})}\hat{\hat{J}}....\hat{\hat{J}}e^{(\hat{\hat{L}}-\hat{\hat{J}})t_1}\rho(0) \tag{18}$$

Reading (18) from right to left, $\hat{\hat{L}} - \hat{\hat{J}}$ can be interpreted as the "between jump" evolution of the system and at t_1 the system experiences a first jump, followed by a period of between jump evolution and so on. $\hat{\hat{J}}$, the jump operator, can be identified with terms bilinear in ρ.

$$\hat{\hat{J}} = \sum_i L_i \bullet L_i^+ \tag{19}$$

$$\hat{\hat{L}} = -iH \bullet + \bullet iH + \sum_i \left(L_i \bullet L_i^+ - \frac{1}{2}L_i^+ L_i \bullet - \frac{1}{2} \bullet L_i^+ L_i \right) \tag{20}$$

$$\begin{aligned} \hat{\hat{L}} - \hat{\hat{J}} &= -iH \bullet + \bullet iH - \sum_i \left(\frac{1}{2}L_i^+ L_i \bullet + \frac{1}{2} \bullet L_i^+ L_i \right) \\ &= -i(H \bullet - \bullet H - \sum_i \left(\frac{i}{2}L_i^+ L_i \bullet + \frac{i}{2} \bullet L_i^+ L_i \right)) \\ &= -i[H - \frac{i}{2}\sum_i L_i^+ L_i, \bullet] \end{aligned} \tag{21}$$

Identifying the fact that if a quantum jump is not executed between time interval t and $t + dt$, $e^{(\hat{\hat{L}}-\hat{\hat{J}})dt}$ propagates the state $\rho(t) \to \rho(t + dt)$.

$$|\psi(t + dt)\rangle = e^{-iH_{eff}dt} |\psi(t)\rangle \tag{22}$$

where

$$H_{eff} = H - \frac{i}{2}\sum_i L_i^+ L_i \tag{23}$$

5

Substituting the jump operators corresponding to (3) and (4), which will be discussed below, into (23) we obtained (10). This shows clearly how the non-Hermitian Hamiltonian is central to the quantum jump formalism. It is Kominis's neglect of this quantity that led to erroneous results.

B. Expression for $d\rho_{incoh}$

If there are no coherences, $\rho = Q_S\rho Q_S + Q_T\rho Q_T$ and equation (7) follows trivially. Writing (6) in the limit $\rho_{coh} = 0$

$$\begin{aligned}
\frac{d\rho}{dt} &= -i[H,\rho] - \frac{k_S + k_T}{2}(\rho Q_S + Q_S\rho - 2Q_S\rho Q_S) - k_S Q_S\rho Q_S - k_T Q_T\rho Q_T \\
&= -i[H,\rho] - \frac{k_S}{2}\{Q_S,\rho\} - \frac{k_T}{2}\{Q_T,\rho\}
\end{aligned}$$

The Jones-Hore equation (9) also reduces to same equation.

C. Expression for $d\rho_{coh}$

The expression for $d\rho_{coh}$ suggests that the total density matrix is removed at the combined rate at which the reactants are transformed to product. This approach is no longer state selective as we know that $|S\rangle \to |T_0\rangle$ and $|T\rangle \to |S_0\rangle$ transitions are forbidden. Hence a differential rate between singlet recombination and triplet recombination should manifest itself in different rates at which the singlet and triplet states are depopulated. This suggests that the expression for $d\rho_{coh}$ is correct only if $k_S = k_T$. In the limit $\rho_{coh} = 1$ and $k_S = k_T = k$, (6) reads

$$\frac{d\rho}{dt} = -i[H,\rho] - k(\rho Q_S + Q_S\rho - 2Q_S\rho Q_S) - (kTr\{Q_S\rho\} + kTr\{Q_T\rho\})\frac{\rho}{Tr\{\rho\}} \quad (24)$$

Knowing that

$$Tr\{\rho\} = Tr\{Q_S\rho\} + Tr\{Q_T\rho\} \quad (25)$$

we find

$$\frac{d\rho}{dt} = -i[H,\rho] - k(\rho Q_S + Q_S\rho - 2Q_S\rho Q_S) - k\rho \quad (26)$$

(26) is exactly equal to the Jones-Hore equation (9) in the same limit.

D. Unphysical Prediction of the Kominis Master Equation

The Kominis master equation predicts that in the absence of singlet-triplet interconversion and $k_T = 0$, starting from a totally coherent mixture of S and T one will have triplet population equal to 0.25 after reaction [6].

Kominis attempted to defend the unexpected fall in $\langle Q_T \rangle$ by analysing a single molecule trajectory. Paraphrasing his argument, at $t = 0$, the radical pair can either react with probability $p_r = k_S dt \langle Q_S \rangle = \frac{k_S dt}{2}$ or not react with probability $p_{nr} = 1 - \frac{k_S dt}{2}$. Conditioned on the fact that the radical pairs do not react, measurement at rate $\frac{k_S}{2}$ causes the singlet projection to occur with probability $q_S = \frac{k_S \langle Q_S \rangle dt}{2} = \frac{k_S dt}{4}$, triplet projection to occur with with probability $q_T = \frac{k_S \langle Q_T \rangle dt}{2} = \frac{k_S dt}{4}$ and the probability of no projection $q_0 = 1 - \frac{k_S dt}{2}$. As pure singlet will react eventually and pure triplet will never react, summing up pure singlet produced by the measurement and singlet product will give the total singlet yield.

$$Y_S = (p_r + p_{nr}q_S) + p_{nr}q_0(p_r + p_{nr}q_S) + (p_{nr}q_0)^2(p_r + p_{nr}q_S)\ldots \tag{27}$$

$$p_{nr}q_0 = \left(1 - \frac{k_S dt}{2}\right)^2 \approx 1 - k_S dt \tag{28}$$

$$p_r + p_{nr}q_S = \frac{k_S dt}{2} + \left(1 - \frac{k_S dt}{2}\right)\frac{k_S}{4}dt \approx \frac{3k_S dt}{4} \tag{29}$$

By summing Y_S, Kominis obtains

$$Y_S = \frac{3k_S dt}{4}\sum_{n=0}^{\infty}(1 - k_S dt)^n = \frac{3}{4} \tag{30}$$

The error in this summing procedure is the fact that the whole density matrix is removed with probability $p_r = k_S dt \langle Q_S \rangle$ to form the singlet product in the first step. This leads to non-conservation of spin angular momentum.

Kominis attempted to circumvent this lack of conservation of spin angular momentum by invoking a time averaged ρ_{coh}. He argues that

$$\rho_{coh}(t) = \frac{\langle\langle Tr\{\rho_{ST}(t)\rho_{TS}(t+\tau)\}\rangle\rangle}{Tr\{\rho_{SS}\}Tr\{\rho_{TT}\}} \tag{31}$$

$$\rho_{TS}(t+\tau) = e^{-iH\tau}\rho_{TS}(t)e^{iH\tau} \tag{32}$$

where $\langle\langle\ldots\rangle\rangle$ indicates time average over τ, with τ being larger than the inverse S-T energy difference and smaller than the characteristic time-scale of the reaction. Assuming the S-T energy separation is J, as e^{-iJt} rotates rapidly around the complex plane

7

$$\rho_{coh}(t) = \frac{\langle\langle Tr\{\rho_{ST}(t)e^{-iJ\tau}\rho_{TS}(t)e^{iJ\tau}\}\rangle\rangle}{Tr\{\rho_{SS}\}Tr\{\rho_{TT}\}} \approx 0 \tag{33}$$

However, (31) is physically questionable. There is no necessary relationship between the S-T energy difference and the characteristic time-scale of the reaction, both are system-dependent parameters.

Furthermore, the validity of (32) is dubious. By integrating the Liouville-von Neuman equation

$$\rho(t+\tau) = e^{-iH\tau}\rho(t)e^{iH\tau} \tag{34}$$

$$\rho_{TS}(t+\tau) = Q_T e^{-iH\tau}\rho(t)e^{iH\tau}Q_S \tag{35}$$

only when $[H, Q_S] = 0$ and $[H, Q_T] = 0$, i.e. in the absence of singlet-triplet interconversion, can the order of the exponentials be reversed, so that (32) is recovered.

E.   Radical-ion-pair reactions and the optical double slit

The introduction of ρ_{coh} and the analogy with the optical double slit experiment suggests that there is singlet interference to triplet product and triplet interference to singlet product. In an optical double slit, the field incident on the screen at position $\overrightarrow{r}$ at time t is the superposition of the fields from the two slits

$$E^{(+)}(\overrightarrow{r}, t) = E_1^{(+)}(\overrightarrow{r}, t) + E_2^{(+)}(\overrightarrow{r}, t) \tag{36}$$

This is because the two slits are physically identical in an optical double slit experiment and a single photon can be diffracted by both slits. In a chemical reaction, spin angular momentum conservation demands that only singlet reactant can enter the "singlet reaction slit" and only triplet reactant can enter the "triplet reaction slit". A superposition state cannot react, the coherence is destroyed as the starting state for the jump is selected from among the stationary states represented in the superposition.

III. CONSISTENT DERIVATION OF MASTER EQUATION USING QUANTUM JUMP APPROACHES

A. Consistent Derivation of Jones-Hore Master Equation

Treating quantum measurement and chemical reaction as quantum jump processes gives a physical interpretation of the Jones-Hore master equation. Using jump operators (37) - (40) , the master equation (9) can be recovered.

$$J_1 = |S_0\rangle\langle S| \tag{37}$$

$$J_2 = |T_0\rangle\langle T| \tag{38}$$

$$J_3 = |T\rangle\langle T| \tag{39}$$

$$J_4 = |S\rangle\langle S| \tag{40}$$

(37) and (38) are the same as (3) and (4) and correspond to quantum jumps to singlet and triplet product respectively. (39) and (40) correspond to a strong measurement of the system, the same intuition that lead to equation (2). The evolution of the wavefunction, $|\psi(t)\rangle \to |\psi(t+dt)\rangle$ is described by

$$
\begin{aligned}
|\psi(t+dt)\rangle &= \frac{e^{-iH_{eff}dt}|\psi(t)\rangle}{\sqrt{\langle\Psi|e^{iH_{eff}^+dt}e^{-iH_{eff}dt}|\Psi\rangle}} & p &= 1 - k_S dt - k_T dt \\
|\psi(t+dt)\rangle = |S_0\rangle &= \frac{J_1|\psi(t)\rangle}{\sqrt{\langle Q_S\rangle}} & p &= k_S\langle Q_S\rangle\, dt \\
|\psi(t+dt)\rangle = |T\rangle &= \frac{J_3|\psi(t)\rangle}{\sqrt{\langle Q_T\rangle}} & p &= k_S\langle Q_T\rangle\, dt \\
|\psi(t+dt)\rangle = |T_0\rangle &= \frac{J_2|\psi(t)\rangle}{\sqrt{\langle Q_T\rangle}} & p &= k_T\langle Q_T\rangle\, dt \\
|\psi(t+dt)\rangle = |S\rangle &= \frac{J_4|\psi(t)\rangle}{\sqrt{\langle Q_S\rangle}} & p &= k_T\langle Q_S\rangle\, dt
\end{aligned}
\tag{41}
$$

The form of the non-Hermitian effective Hamiltonian describing both quantum measurement and chemical reaction (42) follows from (23)

$$
\begin{aligned}
H_{eff} &= H - \frac{i}{2}\sum_i L_i^+ L_i \\
&= H - \frac{i}{2}\left(k_S Q_S + k_T Q_S + k_S Q_T + k_T Q_T\right) \\
&= H - i\frac{k_S + k_T}{2}
\end{aligned}
\tag{42}
$$

9

The interpretation of (41) is that with probability $k_S dt$, the wavefunction attempts to react via the singlet channel and with probability $k_T dt$, the wavefunction attempts to react via the triplet channel. The singlet channel measures the wavefunction and with probability $k_S \langle Q_S \rangle dt$, the wavefuction will react and form singlet product and with probability $k_S \langle Q_T \rangle dt$ the wavefunction will be "measured" and forms a pure triplet, hence fails to react and escapes the singlet recombination channel as a pure triplet. Analogously, with probability $k_T \langle Q_T \rangle dt$ the wavefuction will react and form triplet product and with probability $k_T \langle Q_S \rangle dt$ the wavefunction will be "measured" and form a pure singlet. Expanding (41) and keeping only first order terms in dt, one obtains

$$
\begin{aligned}
\rho(t + dt) = \ &\rho(t) - i[H, \rho] - \tfrac{k_S}{2}\{J_1^+ J_1, \rho(t)\}dt + \tfrac{k_T}{2}\{J_2^+ J_2, \rho(t)\}dt + k_S J_1 \rho(t) J_1^+ dt + k_T J_2 \rho(t) J_2^+ dt \\
&- \tfrac{k_S}{2}(J_3 \rho(t) + \rho(t)J_3 - 2J_3 \rho(t) J_3^+)dt - \tfrac{k_T}{2}(J_4 \rho(t) + \rho(t)J_4 - 2J_4 \rho(t) J_4^+)dt
\end{aligned}
$$

projecting into the S-T basis and making use of the relation $J_3 = 1 - J_4$, equation (9) is recovered.

B.   Derivation of the Traditional Master Equation

The phenomenological master equation can be derived in a way similar to the Jones-Hore master equation, but using different jump operators.

$$
|\psi(t + dt)\rangle = \frac{e^{-iH_{eff}dt}}{\sqrt{\langle \Psi | e^{iH_{eff}^+ dt} e^{-iH_{eff}dt} | \Psi \rangle}} |\psi(t)\rangle \quad p = 1 - k_S \langle Q_S \rangle \, dt - k_T \langle Q_T \rangle \, dt
$$

$$
|\psi(t + dt)\rangle = |S_0\rangle = \frac{J_1 |\psi(t)\rangle}{\sqrt{\langle Q_S \rangle}} \quad p = k_S \langle Q_S \rangle \, dt
$$

$$
|\psi(t + dt)\rangle = |T_0\rangle = \frac{J_2 |\psi(t)\rangle}{\sqrt{\langle Q_T \rangle}} \quad p = k_T \langle Q_T \rangle \, dt \tag{43}
$$

$$
H_{eff} = H - i\frac{k_S}{2}Q_S - i\frac{k_T}{2}Q_T \tag{44}
$$

The interpretation of (43) is that with probability $k_S dt$, the wavefunction attempts to react via the singlet channel and with probability $k_T dt$, the wavefunction attempts to react via the triplet channel. With probabilities $k_S \langle Q_S \rangle \, dt$ and $k_T \langle Q_T \rangle \, dt$ a reaction occurred.

However, *nothing* can be said about reactants that attempt to react but fail to do so. Therefore, a failed reaction doesn't return a pure singlet or triplet [12].

In a qualitative sense, the difference between the two master equations can be described using transition state theory. With a perfectly penetrative barrier, reaching the barrier but not reacting necessarily implies that one is in the wrong spin state, thus the fact that the molecule is in the singlet channel yet does not react is physically significant. With a partially reflective barrier, no reaction doesn't imply the reactant is in the wrong spin state - reactant that is in the correct spin state and reaches the barrier can still get reflected.

Making the analogy between spin-selective chemical reaction and quantum optics, the difference between the quantum measurement master equation and the traditional master equation corresponds to measurement of the state of a quantum optical system via a fluorescence detection experiment or by observing a spontaneous decay process (Fig.1). In fluorescence detection [13], light is shone on the atom to excite it selectively from one of its two ground states, the bright state, into a third excited state, whereupon it spontaneously emits a photon and returns to the original state. The other ground state, the dark state, is not excited by the incident light. Hence if one observes no photon emitted after exciting the system, one is sure that the system is in the dark state and thus null measurement effectively collapses the wavefunction [14, 15].

In the spontaneous emission scenario, two excited states are coherently interconverting and only one state can decay to a ground state. If one observes a photon, a measurement is performed and the wavefunction collapsed onto the bright state before emitting a photon. However, not observing a photon is not physically significant and does not collapse the wavefunction. Of course, not observing a photon for infinitely long time implies that the system is in the ground state, as explained in the previous section.

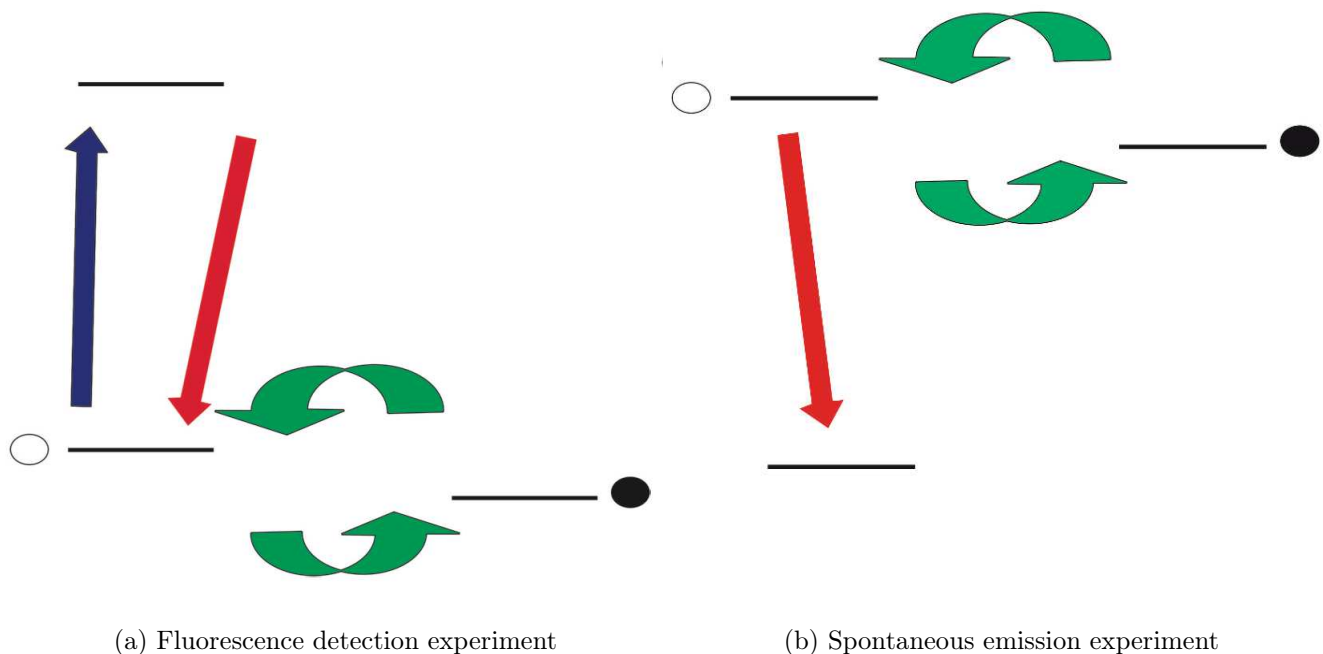(a) Fluorescence detection experiment   (b) Spontaneous emission experiment

Figure 1: Analogy between a quantum optics experiment and a spin-selective reaction. The blue arrow indicates excitation to an excited state, the red arrow indicates radiative decay and the green arrow indicates coherent interconversion between the energy states. The white and black spots indicates dark and bright states respectively.

Acknowledgments

[1] R. Haberkorn, *Mole. Phys.*, 1976, **32**, 1491–1493.

[2] I. K. Kominis, *Phys. Rev. E*, 2009, **80**, 056115.

[3] I. K. Kominis, *Phys. Rev. E*, 2010, **81**, 029901(E).

[4] H. Carmichael, *Phys. Rev. A*, 1997, **56**, 5065–5099.

[5] K. Molmer, Y. Castin, J. Dalibard, *J. Opt. Soc. Am. B*, 1993, **10**, 524–538.

[6] I. K. Kominis, *Phys. Rev. E*, 2011, **83**, 056118.

[7] J. A. Jones, P. J. Hore, *Chem. Phys. Lett.*, 2010, **488**, 90–93.

[8] K. L. Ivanov, M. V. Petrova, N. N. Lukzen, K. Maeda, *J. Phys. Chem. A*, 2010, **114**, 9447–9455.

[9] H. Wiseman, *Quantum and Semicl. Opt.*, 1996, **8**, 205–222.

[10] M. Plenio, P. Knight, *Rev. Mod. Phys.*, 1998, **70**, 101–144.

[11] H. Carmichael, *An open system approach to quantum optics*, Springer Verlag, 1991.

[12] J. A. Jones, K. Maeda, P. J. Hore, *Chem. Phys. Lett.*, 2011, **507**, 269–273.

[13] J. Volz, R. Gehr, G. Dubois, J. Esteve, J. Reichel, *Nature*, 2011, **475**, 210–213.

[14] M. Porrati, S. Putterman, *Phys. Rev. A*, 1987, **36**, 929–932.

[15] W. M. Itano, D. J. Heinzen, J. J. Bollinger, D. J. Wineland, *Phys. Rev. A*, 1990, **41**, 2295.

[16] H. Carmichael, *Statistical Methods in Quantum Optics*, Springer Verlag, 2002.

[17] J. L. Skinner, D. Hsu, *J. Phys. Chem.*, 1986, **90**, 4931.

[18] W. C. Schieve, L. O. Horwitz, *Quantum Statistical Mechanics*, Cambridge University Press, 2009.

Appendix A: Microscopic derivation of the Jones-Hore Master Equation

Following Carmichael [16], the total Hamiltonian is the sum of system, environment and interaction Hamiltonians:

$$H = H_{sys} + H_{env} + H_{int} \tag{A1}$$

Moving to the interaction picture, the Liouville-von Neuman equation is

$$\frac{d\widetilde{\rho}}{dt} = -i[\tilde{H}_{int}, \widetilde{\rho}] \tag{A2}$$

Formal integration gives

$$\widetilde{\rho}(t) = \widetilde{\rho}(0) - i \int\limits_0^t dt'[\tilde{H}_{int}(t'), \widetilde{\rho}(t')] \tag{A3}$$

13

Substituting $\widetilde{\rho}(t)$ back into the right hand side of (A2) gives

$$\frac{d\widetilde{\rho}}{dt} = -i[\tilde{H}_{int}(t), \widetilde{\rho}(0)] - \int_0^t dt'[\tilde{H}_{int}(t), [\tilde{H}_{int}(t'), \widetilde{\rho}(t')]] \tag{A4}$$

Tracing out the reservoir degrees of freedom, and assuming that there are no initial system-reservoir correlations, i.e $tr_R([\tilde{H}_{int}(t), \widetilde{\rho}(0)])$

$$\frac{d\widetilde{\rho}_S(t)}{dt} = -\int_0^t dt' tr_R\left\{[\tilde{H}_{int}(t), [\tilde{H}_{int}(t'), \widetilde{\rho}(t')]]\right\} \tag{A5}$$

where $\widetilde{\rho}_S = tr_R(\rho)$ is the density matrix of the system. In the limit of weak coupling and an infinitely large reservoir, the motion of the system and reservoir remains factored throughout the evolution, hence

$$\widetilde{\rho}(t) = R_0\widetilde{\rho}_S(t) \tag{A6}$$

where R_0 is the initial reservoir state. Substituting in (A5) gives

$$\frac{d\widetilde{\rho}_S(t)}{dt} = -\int_0^t dt' tr_R\left\{[\tilde{H}_{int}(t), [\tilde{H}_{int}(t'), R_0\widetilde{\rho}_S(t')]]\right\} \tag{A7}$$

Writing

$$\tilde{H}_{int} = \sum_i \tilde{\Gamma}_i\widetilde{s}_i \tag{A8}$$

where $\widetilde{\Gamma}_i$ are operators belonging to the reservoir subspace and $\widetilde{s}_i$ are operators belonging to the system space, gives

$$\frac{d\widetilde{\rho}_S(t)}{dt} = -\sum_{i,j}\int_0^t dt' tr_R\left\{[\tilde{\Gamma}_i(t)\widetilde{s}_i(t), [\tilde{\Gamma}_j(t')\widetilde{s}_j(t'), R_0\widetilde{\rho}_S(t')]]\right\} \tag{A9}$$

Expanding out the sum and recognizing reservoir correlation functions, we obtain

$$\frac{d\widetilde{\rho}_S(t)}{dt} = -\sum_{i,j}\int_0^t dt'[\widetilde{s}_i(t)\widetilde{s}_j(t')\widetilde{\rho}_S(t') - \widetilde{s}_j(t')\widetilde{\rho}_S(t')\widetilde{s}_i(t)]\left\langle\tilde{\Gamma}_i(t)\tilde{\Gamma}_j(t')\right\rangle_R + h.c \tag{A10}$$

where

$$\left\langle\tilde{\Gamma}_i(t)\tilde{\Gamma}_j(t')\right\rangle_R = tr_R[R_0\tilde{\Gamma}_i(t)\tilde{\Gamma}_j(t')] \tag{A11}$$

14

The system Hamiltonian, in the $\{S, T, S_0, T_0\}$ basis, is

$$H_{sys} = \begin{pmatrix} \omega_0 & 0 & 0 & 0 \\ 0 & \omega_1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} = \omega_0 J_1^+ J_1 + \omega_1 J_2^+ J_2 \qquad (A12)$$

The environment is assumed to be a series of harmonic oscillators that absorbs the energy dissipated from the system and two measurement devices, which are also modeled as harmonic oscillators

$$H_{env} = \sum_k \omega_k a_{k,1}^+ a_{k,1} + \sum_k \omega_k a_{k,2}^+ a_{k,2} + \omega_b \sum_k b_k^+ b_k + \omega_c \sum_k c_k^+ c_k \qquad (A13)$$

The interaction Hamiltonian comprises two parts, a dissipative part (H_{diss}) which is modeled as the Jaynes-Cumming Hamiltonian [16] and a measurement Hamiltonian (H_{mea}) [17].

$$H_{diss} = \sum_k (g_k a_{k,1}^+ J_1 + g_k^* a_{k,1} J_1^+) + \sum_{k'} (q_{k'} a_{k',2}^+ J_2 + q_{k'}^* a_{k',2} J_2^+) \qquad (A14)$$

$$H_{mea} = J_1^+ J_1 \sum_k (\alpha_k b_k^+ + \alpha_k^* b_k) + J_2^+ J_2 \sum_{k'} (\beta_{k'} c_{k'}^+ + \beta_{k'}^* c_{k'}) \qquad (A15)$$

The measurement device b measures the singlet occupancy and the device c measures the triplet occupancy. Note that $[H_{sys}, H_{mea}] = 0$ and $[H_{sys}, H_{diss}] \neq 0$, implying that energy is conserved by the measurement process but not conserved by the dissipative dynamics. Looking at the form of the measurement Hamiltonian, at long times, the measurement devices b and c will collapse to pointer states $J_1^+ J_1$ and $J_2^+ J_2$ respectively [18]. Let

$$\widetilde{\Gamma}_{A,1} = \sum_k g_k^* a_{k,1} e^{-i\omega_k t} \qquad (A16)$$

$$\widetilde{\Gamma}_{A,2} = \sum_k q_k^* a_{k,2} e^{-i\omega_k t} \qquad (A17)$$

$$\widetilde{\Gamma}_B = \sum_k \alpha_k^* b_k e^{-i\omega_k t} \qquad (A18)$$

$$\widetilde{\Gamma}_C = \sum_k \beta_k^* c_k e^{-i\omega_k t} \qquad (A19)$$

Writing out explicitly the operators in the form of (A8)

$$\widetilde{\Gamma}_1 = \widetilde{\Gamma}_{A,1}^+ \qquad \widetilde{s}_1 = J_1 e^{-i\omega_0 t}$$

$$\widetilde{\Gamma}_2 = \widetilde{\Gamma}_{A,1} \qquad \widetilde{s}_2 = J_1^+ e^{i\omega_0 t}$$

$$\widetilde{\Gamma}_3 = \widetilde{\Gamma}_{A,2}^+ \qquad \widetilde{s}_3 = J_2 e^{-i\omega_1 t}$$

$$\widetilde{\Gamma}_4 = \widetilde{\Gamma}_{A,2} \qquad \widetilde{s}_4 = J_2^+ e^{i\omega_1 t}$$

$$\widetilde{\Gamma}_5 = \widetilde{\Gamma}_B + \widetilde{\Gamma}_B^+ \qquad \widetilde{s}_5 = J_1^+ J_1$$

$$\widetilde{\Gamma}_6 = \widetilde{\Gamma}_C + \widetilde{\Gamma}_C^+ \qquad \widetilde{s}_6 = J_2^+ J_2$$

At zero temperature, reservoirs A_1, A_2, B and C have the following correlation functions

$$\left\langle \tilde{\Gamma}(t)\tilde{\Gamma}(t') \right\rangle_R = 0 \tag{A20}$$

$$\left\langle \tilde{\Gamma}^+(t)\tilde{\Gamma}^+(t') \right\rangle_R = 0 \tag{A21}$$

$$\left\langle \tilde{\Gamma}^+(t)\tilde{\Gamma}(t') \right\rangle_R = 0 \tag{A22}$$

$$\left\langle \tilde{\Gamma}(t)\tilde{\Gamma}^+(t') \right\rangle_R = \sum_j |k_j|^2 \, e^{-i\omega_j(t-t')} = \int_0^\infty d\omega \, |k(\omega)|^2 \, g(\omega) e^{-i\omega(t-t')} \tag{A23}$$

where k_j is the generic system-reservoir coupling constant, and $g(\omega)$ is the density of states in the continuum limit. Substituting and noting that the S and T states are orthogonal and reservoirs A_1, A_2, B and C are uncorrelated and thus statistically independent

$$\begin{aligned}
\frac{d\widetilde{\rho}_S(t)}{dt} = {} & \int_0^t dt' [J_1^+ J_1 \widetilde{\rho}_S(t') - J_1 \widetilde{\rho}_S(t') J_1^+] e^{-i\omega_0(t-t')} \left\langle \tilde{\Gamma}_{A,1}(t)\tilde{\Gamma}_{A,1}^+(t') \right\rangle_R \\
& + [J_2^+ J_2 \widetilde{\rho}_S(t') - J_2 \widetilde{\rho}_S(t') J_2^+] e^{-i\omega_1(t-t')} \left\langle \tilde{\Gamma}_{A,2}(t)\tilde{\Gamma}_{A,2}^+(t') \right\rangle_R \\
& + [J_1^+ J_1 \widetilde{\rho}_S(t') - J_1^+ J_1 \widetilde{\rho}_S(t') J_1^+ J_1] \left\langle \tilde{\Gamma}_B(t)\tilde{\Gamma}_B^+(t') \right\rangle_R \\
& + [J_2^+ J_2 \widetilde{\rho}_S(t') - J_2^+ J_2 \widetilde{\rho}_S(t') J_2^+ J_2] \left\langle \tilde{\Gamma}_C(t)\tilde{\Gamma}_C^+(t') \right\rangle_R + h.c \tag{A24}
\end{aligned}$$

Substituting $\tau = t - t'$

$$\frac{d\widetilde{\rho}_S(t)}{dt} = \int_0^t d\tau [J_1^+ J_1 \widetilde{\rho}_S(t-\tau) - J_1 \widetilde{\rho}_S(t-\tau) J_1^+] e^{-i\omega_0\tau} \left\langle \tilde{\Gamma}_{A,1}(t)\tilde{\Gamma}_{A,1}^+(t-\tau) \right\rangle_R$$
$$+ [J_2^+ J_2 \widetilde{\rho}_S(t-\tau) - J_2 \widetilde{\rho}_S(t-\tau) J_2^+] e^{-i\omega_1\tau} \left\langle \tilde{\Gamma}_{A,2}(t)\tilde{\Gamma}_{A,2}^+(t-\tau) \right\rangle_R$$
$$+ [J_1^+ J_1 \widetilde{\rho}_S(t-\tau) - J_1^+ J_1 \widetilde{\rho}_S(t-\tau) J_1^+ J_1] \left\langle \tilde{\Gamma}_B(t)\tilde{\Gamma}_B^+(t-\tau) \right\rangle_R$$
$$+ [J_2^+ J_2 \widetilde{\rho}_S(t-\tau) - J_2^+ J_2 \widetilde{\rho}_S(t-\tau) J_2^+ J_2] \left\langle \tilde{\Gamma}_C(t)\tilde{\Gamma}_C^+(t-\tau) \right\rangle_R + h.c \quad \text{(A25)}$$

Performing the Markov approximation and replacing $t - \tau$ terms in the density operator by t

$$\frac{d\widetilde{\rho}_S(t)}{dt} = [J_1^+ J_1 \widetilde{\rho}_S(t) - J_1 \widetilde{\rho}_S(t) J_1^+] \int_0^t d\tau e^{-i\omega_0\tau} \left\langle \tilde{\Gamma}_{A,1}(t)\tilde{\Gamma}_{A,1}^+(t-\tau) \right\rangle_R$$
$$+ [J_2^+ J_2 \widetilde{\rho}_S(t) - J_2 \widetilde{\rho}_S(t) J_2^+] \int_0^t d\tau e^{-i\omega_1\tau} \left\langle \tilde{\Gamma}_{A,2}(t)\tilde{\Gamma}_{A,2}^+(t-\tau) \right\rangle_R$$
$$+ [J_1^+ J_1 \widetilde{\rho}_S(t) - J_1^+ J_1 \widetilde{\rho}_S(t) J_1^+ J_1] \int_0^t d\tau \left\langle \tilde{\Gamma}_B(t)\tilde{\Gamma}_B^+(t-\tau) \right\rangle_R$$
$$+ [J_2^+ J_2 \widetilde{\rho}_S(t) - J_2^+ J_2 \widetilde{\rho}_S(t) J_2^+ J_2] \int_0^t d\tau \left\langle \tilde{\Gamma}_C(t)\tilde{\Gamma}_C^+(t-\tau) \right\rangle_R + h.c. \quad \text{(A26)}$$

Ignoring imaginary frequency shifts, one can define

$$\int_0^t d\tau e^{-i\omega_0\tau} \left\langle \tilde{\Gamma}_{A,1}(t)\tilde{\Gamma}_{A,1}^+(t-\tau) \right\rangle_R = \int_0^t d\tau \left\langle \tilde{\Gamma}_B(t)\tilde{\Gamma}_B^+(t-\tau) \right\rangle_R = \frac{k_S}{2} \quad \text{(A27)}$$

$$\int_0^t d\tau e^{-i\omega_1\tau} \left\langle \tilde{\Gamma}_{A,2}(t)\tilde{\Gamma}_{A,2}^+(t-\tau) \right\rangle_R = \int_0^t d\tau \left\langle \tilde{\Gamma}_C(t)\tilde{\Gamma}_C^+(t-\tau) \right\rangle = \frac{k_T}{2} \quad \text{(A28)}$$

$$\frac{d\widetilde{\rho}_S(t)}{dt} = -\frac{k_S}{2}(J_1^+ J_1 \widetilde{\rho}_S(t) + \widetilde{\rho}_S(t) J_1^+ J_1 - 2J_1 \widetilde{\rho}_S(t) J_1^+) - \frac{k_T}{2}\left(J_2^+ J_2 \widetilde{\rho}_S(t) - \widetilde{\rho}_S(t) J_2^+ J_2 - 2J_2 \widetilde{\rho}_S(t) J_2^+\right)$$
$$-\frac{k_s + k_T}{2}\left(J_1^+ J_1 \widetilde{\rho}_S(t) + \widetilde{\rho}_S(t) J_1^+ J_1 - 2J_1^+ J_1 \widetilde{\rho}_S(t) J_1^+ J_1\right) \quad \text{(A29)}$$

Converting back to the Schrödinger picture and projecting into {S,T} subspace, (9) is recovered.